THERMAL CONDUCTIVITY OF SULPHURDIOXIDE AND DIETHYL ETHER AT DIFFERENT TEMPERATURES

A. DAS GUPTA

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,

CALCUTTA-32.

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ABSTRACT. Thermal conductivity of sulphurdioxide and diethyl ether have been measured over the temperature range 39°-200.6°C with the help of thick-wire variant of the hot wire method. The observed data are in good agreement with the results obtained by earlier workers. Attempt has been made to interpret the observed data in the light of the recent theory developed by Mason and Monchick. It is found that relaxation phenomenon plays a significant role in the interchange of energy between translational and rotational degrees of freedom.

INTRODUCTION

Besides being of industrial and technological importance accurate measurements of thermal conductivity of polyatomic gases may serve as a source of information regarding the interchange of energy between internal and external degrees of freedom. Unlike monatomic gases which are devoid of internal motions, the heat conductivity of a polyatomic gas cannot be explained with the help of the classical theory. (Hirschfelder, Curtiss and Bird, 1954). The first attempt to take into consideration the transport of internal energy was made by Eucken (1913) according to whom,

$$\lambda M/\eta = f_{tr}Cv_{tr}+f_{int}Cv_{int} \qquad \ldots (1)$$

where λ = coefficient of thermal conductivity, η = coefficient of viscosity, M is the molecular mass, Cv_{tr} and Cv_{int} are the translational heat capacity and the internal heat capacity respectively. f_{tr} and f_{int} are the Eucken factors corresponding to the translational and internal degrees of freedom. For the noble gases f_{tr} was assigned a value 5/2 while from mean free path arguments f_{int} was taken to be equal to 1. Experiment, however, shows that f_{int} is temperature dependent for most of the polyatomic gases and varies from 0.7 to 1.3 over the temperature range 80°K — 380°K. It was suggested later by several workers that transport of internal energy takes place by some diffusion mechanism and f_{int} should be replaced by $\rho D/\eta$ where ρ is the gas density and D the self-diffusion coefficient. A more rigorous attempt to derive explicit expression for the thermal conductivity of polyatomic gases was made by Hirschfelder (1957) who considered the molecules in different quantum states as different chemical species. According

to him when the exchange of energy between translational and internal degrees of freedom is very fast so that a condition of local chemical equilibrium is maintained, one obtains the modified Eucken expression for the thermal conductivity of a polyatomic gas. Usually, however, for most of the polyatomic gases the condition of local chemical equilibrium is not maintained and it has been felt by several workers (Waelbroeck, and Zuckerbrodt, 1958; Srivastava and Barua, 1960) that some relationship must exist between thermal conductivity and the rate of exchange of energy between translational and the various internal degrees of freedom. The theory of heat conductivity therefore needs a better theoretical foundation so that it can be extended to the case of non-spherical molecules (both polar and nonpolar) undergoing inelastic collision.

Recently Mason and Monchick (1962) have derived explicit expressions for the thermal conductivity of both polar and non polar gases starting from the semi-classical theory of Wang Chang and Uhlenbeck (1964) and making some crude approximations. According to them in the case of nonpolar polyatomic gases a relaxation of energy transfer between translational and internal degrees of freedom affects the transport of heat energy. For polar gases, however, a second effect namely resonant exchange of energy between internal degrees of freedom plays a significant role. Mason and Monchick (1962) derived the following expressions for f_{tr} and f_{int} in the case of a polar gas;

$$f_{tr} = \frac{5}{2}\left[1-\left(\frac{10}{3\pi}\right)\left(1-\frac{2}{5}\frac{\rho D_{int}}{\eta}\right)\frac{1}{R}\Sigma\frac{C_k}{Z_k}\right] \quad \ldots (2)$$

$$f_{int} = \frac{\rho D_{int}}{\eta}\left[1+\frac{5}{\pi}\left(1-\frac{2}{5}\frac{\rho D_{int}}{\eta}\right)\frac{1}{C_{int}}\Sigma\frac{C_k}{Z_k}\right] \quad \ldots (3)$$

$$D_{int} = D[1+Z'/Z_0]^{-1} \quad \ldots (4)$$

In the above expressions C_k is the heat capacity for the K-th internal mode and Z_k is the corresponding collision number . Z'/Z_0 is the correction due to the resonant exchange of internal energy. Generally, however, only the rotational modes are considered since Z is large for other modes. Finally the expression for the heat conductivity of a polar gas becomes,

$$\lambda M/\eta C_V = \frac{1}{C_v}\left[\frac{5}{2}C_{vtr}+\frac{\rho D_{int}}{\eta}C_{v_{int}}-\frac{2}{\pi}\left(\frac{5}{2}-\frac{\rho D_{int}}{\eta}\right)^2\frac{C_{rot}}{Z_{rot}}\right] = f_{M\text{-}M} \ldots (5)$$

where f_{M-M} is the expression for Eucken factor according to Mason and Monchick's formulation.

In the present paper the observed thermal conductivity data have been utilised to determine the Z_{rot} values at different temperatures. In order to study the efficiency of transfer of translational as well as internal energies f_{tr} and f_{in}

values have been determined at different temperatures using the calculated values of Z_{rot}.

APPARATUS AND THEORY

In the present measurement the thick-wire variant of the hot-wire method has been utilised. The description of the conductivity cell has already been given in an earlier paper (Srivastava and Das Gupta, 1966). During experiment the cell was placed in oil bath whose temperature control was in general within $\pm 0.05°C$. The constants of the cell used are given in Table 1.

Gaseous Sulphurdioxide used in this experiment was prepared by the action of concentrated Sulphric acid on Sodium sulphite. The gas was properly dried before use by passing it through Calcium Chloride. Gaseous diethyl ether was obtained by vaporizing chemically pure liquid ether.

The solution of the differential equation for the flow of heat along a wire has been shown by Kannuluik and Martin (1933, 1934) to be as follows,

$$f(\beta l) = (1/\beta l)^2 \left(1 - \frac{\tanh \beta l}{\beta l}\right) = \frac{2\pi r_1^2 \lambda J (R - R_0)}{R_0^2 I^2 \alpha l} \quad \ldots (6)$$

$$\beta^2 = \frac{2h}{r_1 \lambda} - \frac{I^2 R_0 \alpha}{2\pi r_1^2 \lambda J l} \quad \ldots (7)$$

$$h = \frac{K_u}{r_1 \ln (r_2/r_1)} \quad \ldots (8)$$

where R is the resistance of the wire when a current I amp is flowing through it, R_0 is the resistance of the cell wire at the bath temperature for $I = 0$. K_u and λ are the thermal conductivities of the wire and the gas respectively.

In Table II a typical set of observations taken at 80.1°C for SO_2 and $(C_2H_5)_2O$ has been recorded. In this table K_u is the apparent thernal conductivity and K' is that obtained after reduction to the bath temperature and making correction for non-radial flow, radiation loss, temperature jump and wall effects. λ is the thermal conductivity obtained after correcting the mean value of K' for the assymetry in the cell construction by the relation $\lambda = K'(1-C)$. The factor $(1-C)$ was obtained by calibrating the cell with neon at 39°, 80°, 120.3°, 160.5° and 200.8°C taking the data of Kannuluik and Carman (1952) as standard. At every temperature the conductivity has been measured for three different currents and K_u values are found to agree within less than 1% on the average. The thermal conductivity values thus obtained are recorded in Table III. The variation of thermal conductivity with temperature has been shown graphically in Fig. 1. The results obtained for SO_2 and $(C_2H_5)_2O$ are found to be in good agreement with those obtained by Baker and De Haas (1964) and Vines and Bennett (1954) respectively.

TABLE I

Constants of thermal conductivity cell at different temperatures.

Constants/T°C →	39	80	120.3	160.5	200.8
Thermal Conductivity 'λ' of the wire in cal/cm. sec. °C.	0.1670	0.1703	0.1731	0.1748	0.1756
Temperature coefficient of resistance 'α' of the platinum wire in $°C^{-1}$	0.00300	0.00264	0.00239	0.00217	0.00199
Resistance of the cell wire in ohms.	0.9705	1.0927	1.2081	1.3251	1.4416
Cell Constant (1-C)	.987	.985	.985	.985	.985
Length of the cell wire ($2l$)				6.290 cm.	
Radius of the cell wire (r_1)				0.00506 cm.	
Internal diameter of the cell ($2r_2$)				0.301 cm.	
Outer diameter of the cell ($2r_3$)				0.590 cm.	

TABLE II

Observations taken for the thermal conductivity in cal/cm.sec°C at 80.1°C

Substance	I in mA	$(R-R_0)$ in Ω	$K_u \times 10^5$	$K' \times 10^5$	$K'_{mean} \times 10^5$	$\lambda \times 10^5$
	130.03	0.03178	0.032	2.908		
Sulphur	129.29	0.03142	3.031	2.908	2.908	2.893
dioxide	128.25	0.03092	3.030	2.909		
	127.23	0.01914	4.926	4.792		
Diethyl ether	127.84	0.01928	4.938	4.803	4.804	4.774
	129.33	0.01967	4.956	4.818		

COMPARISON WITH THEORY

From eqn. (5) the expression for Z_{rot} becomes,

$$Z_{rot} = \frac{3}{\pi}\left(\frac{5}{2} - \frac{\rho D_{int}}{\eta}\right)^2 \frac{R}{C_v}\left[\frac{\rho D_{int}}{\eta} + \frac{3}{2}\left(\frac{5}{2} - \frac{\rho D_{int}}{\eta}\right)\frac{R}{C_v} - f_{M-M}\right]^{-1} \quad \ldots \quad (9)$$

For the calculation of Z_{rot} from the above equation one must know the values of f_{M-M}, Z'/Z_0, C_v and $\rho D/\eta$ at different temperatures. f_{M-M} occurring in the above expression has been replaced by f_{exp} ($= \lambda M/\eta C$) in the present calculation. The specific heats C_v for SO_2 and $(C_2H_5)_2O$ have been taken from the data of Lambert and Slater (1957) and Vines and Bennett (1954) respectively. It was shown by Baker and De Haas (1964) that for SO_2 Z'/Z_0 is very small and can be

neglected. There being no experimental data for the moment of inertia of diethyl either, it is not possible to determine Z'/Z_0 in this case. This difficulty however, has been avoided by treating weakly polar diethyl ether as a nonpolar polyatomic gas for which D_{int} can be taken to be equal to D the self-diffusion coefficient.

For the calculation of $\rho D/\eta$ the force parameters on 12-6-3 potential given by Mason and Monchick (1961) have been utilised. The viscosity values for SO_2 have been taken from the recent measurements of Pal and Barua (1966) while for $(C_2H_5)_2O$ the data obtained by Craven and Lambert (1951) are utilised. The rotational collision numbers Z_{rot} thus determined have been recorded in column 4 of Table III. These values have been utilised to calculate f_{int} and f_{trans} using the equations (2) and (3).

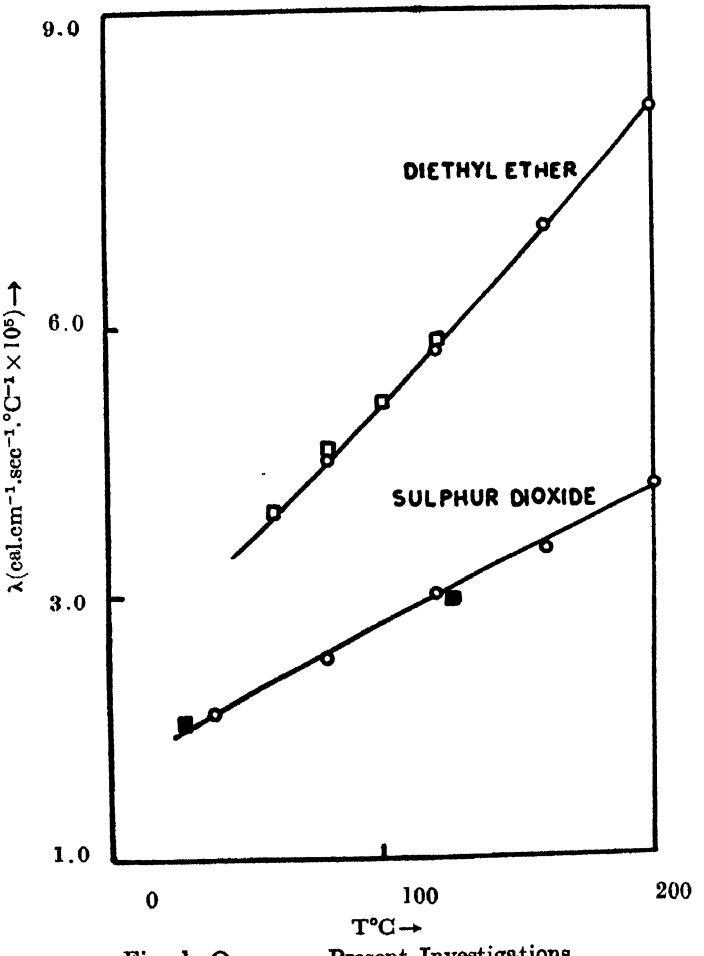

Fig. 1. O————Present Investigations.

□————Vines and Bennett (1954).

Solid □————Baker and De Haas (1964).

TABLE III

Rotational Collision number at different temperatures

Substance	T°C	$\lambda_{expt} \times 10$	Z_{rot}	$f$tr	$f$int
	39.0	2.374	1.08	0.76	1.91
	80.1	2.893	1.13	0.84	1.80
Sulphur dioxide	121.3	3.511	1.29	1.05	1.75
	161.1	3.989	1.49	1.24	1.67
	200.6	4.530	2.00	1.56	1.57
	80.1	4.774	1.12	0.83	1.43
Diethyl ether	120.2	5.806	1.36	1.13	1.40
	160.1	6.945	1.48	1.24	1.38
	200.1	8.095	1.56	1.30	1.37

DISCUSSION

It is evident from the present investigation that the Z_{rot} values obtained from the thermal conductivity measurements show an increase with temperature. This is, however, in accordance with the results obtained for Sulphur dioxide and ammonia by Baker *et al* (1964) and Srivastava and Das Gupta (1966) respectively. Recently Baker and Brokaw (1965) have obtained the reverse result regarding the temperature variation of Z_{rot} for a few polar gases including ammonia using thermal conductivity data. From the formulation of Mason and Monchick (1962) it appears that the rotational collision number is very much sensitive to thermal conductivity results. Hence a slight difference in the temperature dependence of thermal conductivity may yield an entirely different temperature variation for Z_{rot}. Recently, Zink, Bose and Itterbeck (1965, 1966) obtained a decrease in Z_{rot} values with the increase of temperature for Oxygen and Hydrogen-Helium systems, from ultrasonic measurements. In the case of polar gases however, no such experiments have yet been performed. For a polar gas it is rather difficult to predict anything regarding the temperature dependence of Z_{rot} since it involves long range dipole interaction which plays a significant role in energy interchange during collision. Moreover, the temperature variation of Z_{rot} for repulsive interaction is in the opposite direction from that for an attractive interaction. The different theories so far developed give conflicting results regarding the temperature dependence of rotational collision number. Therefore under the circumstances it appears that direct experiments are to be performed for polar gases over a wide range of temperature in order to get some idea about the temperature dependence of translational-rotational energy exchange.

From Table III it can be seen that f_{tr} values increase with the increase of temperature for both the gases whereas f_{int} shows a decrease. This implies that at high temperature the efficiency of translation-rotation energy interchange is reduced. Vines and Bennett (1954) however observed an increase of f_{int} with temperature for some polar and nonpolar polyatomic gases. They attached more importance to the translational-vibrational energy exchange which is usally significant at appreciably high temperatures. At moderate temperature, however the translational-rotational energy exchange plays a more prominent role. Moreover, in the treatment of Vines and Bennett (1954) there was no scope for taking into account the relaxation phenomena in the interchange of energy between external and internal degrees of freedom.

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REFERENCES

Baker, C. B., and de Haas, N., 1964, *Phys. Fluids*, **7**, 1400.

Baker, C. B., and Brokaw, R. S., 1965, *J. Chem. Phys.*, **43**, 3519.

Craven, P. M., and Lambert, J. D., 1951, *Proc. Roy. Soc.* (*London*), *A* **205**, 439.

Eucken, A., 1913, *Z. Physik*, **14**, 324.

Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., 1954, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York.

Hirschfelder, J. O., 1957, Sixth Symposium (International) on Combustion. (Reinhold Publishing Corporation, New York), p. 361.

Kannuluik, W. G., and Martin, L. H., 1933, *Proc. Roy. Soc.* (*London*), *A* **141**, 144; ibid, 1934, *A* **144**, 496.

Kannuluik, W. G., and Carman, E. A., 1952, *Proc. Phys. Soc.*, *B***65**, 701.

Lambert, J. D., and Slater, R., 1957, *Proc. Roy. Soc.* (*London*), *A* **243**, 78.

Mason, E. A., and Monchick, L., 1962, *J. Chem. Phys.*, **36**, 1622.

Monchick, L., and Mason, E. A., 1961, *J. Chem. Phys.*, **35**, 1676.

Pal, A., and Barua, A. K., 1966, *Trans. Faraday Soc.*, **63**, 341.

Srivastava, B. N., and Barua, A. K., 1960, *J. Chem. Phys.*, **32**, 427.

Srivastava, B. N., and Das Gupta, A., 1966, *Phys. Fluids*, **9**, 722.

Vines, R. G., and Bennett, L. A., 1954, *J. Chem. Phys.*, **22**, 360.

Waelbroeck, F. G., and Zuckerbrodt, P., 1958, *J. Chem. Phys.*, **30**, 524.

Wang Chung, C. S., Uhlenbeck, G. E., and de Boer, J., 1964, *Studies in Statistical Mechanics* (North Holland Publishing Company, Amsterdam), Vol. II, 249.

Zink, H., Bose, T. K., and Itterbeek, A., 1965, *Phys. Letters*, **16**, 34.

———————, 1966, *Phys. Letters*, **19**, 642.